

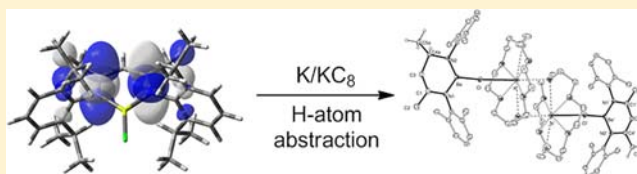
Three-Coordinate Beryllium β -Diketiminates: Synthesis and Reduction Chemistry

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S Supporting Information

ABSTRACT: A series of mononuclear, heteroleptic beryllium complexes supported by the monoanionic β -diketiminato ligand $[\text{HC}\{\text{CMeNDipp}\}_2]^-$ (L; Dipp = 2,6-diisopropylphenyl) have been synthesized. Halide complexes of the form $[\text{LBeX}]$ (X = Cl, I) and a bis(trimethylsilyl)amide complex were produced via salt metathesis routes. Alkylberyllium β -diketiminato complexes of the form $[\text{LBeR}]$ (R = Me, ⁿBu) were obtained by salt metathesis from the chloride precursor $[\text{LBeCl}]$. Controlled hydrolysis of $[\text{LBeMe}]$ afforded an air-stable, monomeric β -diketiminatoberyllium hydroxide complex. $[\text{LBeMe}]$ also underwent facile protonolysis with alcohols to form the corresponding β -diketiminatoberyllium alkoxides $[\text{LBeOR}]$ (R = Me, ⁿBu, Ph). High temperatures and prolonged reaction times were required for protonolysis of $[\text{LBeMe}]$ with primary amines to yield the β -diketiminatoberyllium amide complexes $[\text{LBeNHR}]$ (R = ⁿBu, CH₂Ph, Ph). No reactions were observed between $[\text{LBeMe}]$ and silanes, terminal acetylenes, or secondary amines. All compounds were characterized by ¹H, ¹³C, and ⁹Be NMR spectroscopy and, in most cases, by X-ray crystallography. Reduction of the beryllium chloride complex with potassium metal resulted in apparent hydrogen-atom transfer between two β -diketiminato backbones, yielding two dimeric, potassium chloride bridged diamidoberyllium species. X-ray analysis of a cocrystallized mixture of the 18-crown-6 adducts of these species allowed unambiguous identification of the two reduced diketiminato ligands, one of which had been deprotonated at a backbone methyl substituent and the other reduced by hydride addition to the β -imine position. It is proposed that this process occurs by the formation of an unobserved radical anion species and intermolecular hydrogen-atom transfer by a radical-based hydrogen abstraction mechanism.

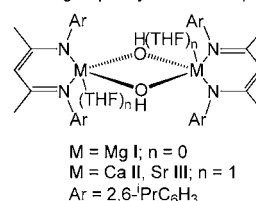


INTRODUCTION

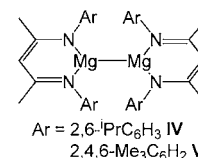
Monoanionic β -diketiminato ligands have long been used for their strong N-donor chelating properties and ease of synthesis, which allows facile tuning of both their steric and electronic properties.^{1,2} Over the past decade, the sterically demanding $[\text{HC}\{\text{CMeNDipp}\}_2]^-$ ligand (L; Dipp = 2,6-diisopropylphenyl) has become the ligand of choice for the stabilization of numerous heteroleptic alkaline-earth complexes of the form $[\text{LMX}]_n$ (M = Mg, Ca, Sr, Ba; X = halide, alkyl, alkoxide, amide, etc.; n = 1–3). Dimeric magnesium β -diketiminato complexes of even the smallest functionalities, such as hydride, fluoride, and hydroxide,³ as well as the analogous dinuclear calcium hydride, amide, cyanide, fluoride, and hydroxide complexes⁴ and strontium fluoride and hydroxide dimers, have thus been isolated.⁵ The alkylmagnesium derivatives $[\text{LMgR}]$ (R = Me, ⁿBu) and the heavier group 2 bis(trimethylsilyl)amides $[\text{LM}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})]$ (M = Ca, Sr), in particular, have found applications in numerous catalytic reactions ranging from polymerization to heterofunctionalization of multiple bonds and dehydrocoupling reactions.⁶ In a notable landmark synthesis of 2007, β -diketiminato ligands also allowed isolation of the first magnesium(I) dimers, compounds IV and V, by Jones and co-workers.⁷

While the heavier group 2 congeners have thus received increased attention over the past decade, the analogous chemistry for beryllium has been largely neglected, primarily because of the

Series of β -diketiminato stabilized heavier group 2 hydroxide complexes



β -diketiminato magnesium(I) complexes



high toxicity of most beryllium precursors and complexes. Although beryllium complexes with N-donor ligands are well precedented,^{8a–c} only a single example of a β -diketiminatoberyllium complex has been reported to date.^{8f} As the smallest of the alkaline-earth dications (six-coordinate ionic radii: Ca²⁺, 1.00 Å; Mg²⁺, 0.72 Å; Be²⁺, 0.45 Å),⁹ beryllium, in contrast to its heavier group 2 congeners, is known to engage in highly covalent bonding. Consequently, its complexes are much less prone to dimerization or Schlenk-type ligand redistribution processes.

Herein we describe the synthesis and characterization of a series of kinetically stable, monomeric β -diketiminatoberyllium complexes and the reduction of their halide derivatives.

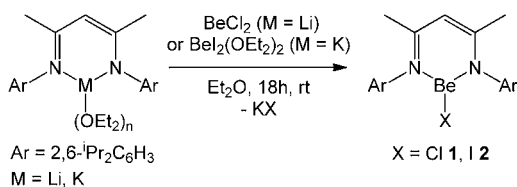
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RESULTS AND DISCUSSION

Halide Complexes. Complex [LBeCl] (1) was synthesized by the reaction of [LLi(OEt₂)] with an equimolar amount of BeCl₂ in diethyl ether at room temperature (Scheme 1). Extraction and

Scheme 1



filtration in hot toluene followed by concentration in vacuo yielded a crop of large colorless crystals of compound 1 after 18 h at room temperature (86% yield). When performed in tetrahydrofuran (THF), the reaction yielded the THF adduct [LBeCl(THF)]. Similarly, complex [LBeI] (2) was obtained by the reaction of LH with [KN(SiMe₃)₂] followed by the addition of BeI₂ in diethyl ether. Filtration from the precipitated KI byproduct and concentration of the diethyl ether filtrate yielded complex 2 as a colorless crystalline solid (85% yield). Performing the synthesis in THF did not provide the THF adduct presumably because the larger size of the iodide substituent precludes coordination of further neutral ligands. Both complexes presented no appreciable solubility in hexanes and were only sparingly soluble in aromatic solvents such as benzene and toluene. ¹H NMR spectroscopic analysis confirmed the clean formation of compounds 1 and 2, while the chemical shifts associated with the β-diketiminato ligand were little affected by the nature of the halide coligand, differing by a maximum of only 0.06 ppm. ⁹Be NMR spectra of compounds 1 and 2 displayed broad singlets at 12.2 and 13.4 ppm, respectively. The upfield shift of the ⁹Be resonance from chloride to iodide most likely reflects the lower electronegativity of the heavier halide and consequent increased shielding of the beryllium atom.

Crystals of 1 and 2 suitable for X-ray structural analysis were obtained by room temperature crystallization from the saturated toluene and diethyl ether filtrates, respectively. The results of these two experiments are displayed in Figure 1, and details of the X-ray analyses and selected bond distance and angle data are provided in Tables 1 and 2, respectively. In contrast to the majority of β-diketiminato complexes of the heavier alkaline-earth metals (Mg, Ca, Sr, Ba) in which the six-membered ring formed by the ligand backbone and the metal center adopted an envelope or boat conformation, the β-diketiminato framework in both complexes 1 and 2 is entirely planar owing to the very small size of the three-coordinate

beryllium dication (0.16 Å). Consistent with a previously noted preference for the smallest alkaline-earth dication to engage in exclusive σ-type interactions with N-donor ligands,^{8b} the beryllium centers of compounds 1 and 2 are thus trigonal-planar and lie in the same plane as the ligand backbones. Both molecules only deviate slightly from C_{2v} symmetry, with the mirror plane passing through the C3–Be–X axis (1, X = Cl; 2, X = I) perpendicular to the ligand framework. Bond lengths and angles of the ligand backbone vary little between the chloride and iodide analogues, demonstrating the rigidity of the β-diketiminato framework (Table 2). The Be–Cl bond length in 1 [1.9041(17) Å] is comparable to that reported by Niemeyer and Power for their similarly three-coordinate terphenylberyllium chloride ether solvate [1.905(3) Å] and those of a recently reported mononuclear beryllium dichloride carbene adduct, IPrBeCl₂ [IPr = 1,3-(diisopropylphenyl)imidazol-1-ylidene] [1.881(6) and 1.884(9) Å].¹⁰ The bond distances around the beryllium center in the iodo complex 2 [Be–I 2.2872(15) Å; Be–N1 1.6032(18) Å; Be–N2 1.6046(18) Å] are comparable to those in the mesityl-substituted β-diketiminato analogue reported by Jones and co-workers [Be–I 2.296(2) Å; Be–N 1.600(2) Å], while the widening of the β-diketiminato bite angle N1–Be–N2 [2; 112.95(10)°] reflects the higher steric demands of the 2,6-diisopropylphenyl substituents compared to the mesityl analogue [111.8(2)°].⁸

Alkyl Complexes. Complexes of the formula [LBeR] (R = 3, Me; 4, *n*Bu) were synthesized by the reaction of the ligand precursor LH with “BeR₂”, which was generated in situ by the addition of 2 equiv of methyllithium or *n*-butyllithium to a slurry of BeCl₂ in diethyl ether at –78 °C (Scheme 2). Alternatively, 3 and 4 could be obtained by the consecutive treatment of the lithium complex [LLi(OEt₂)] with 1 equiv of BeCl₂ and 1 equiv of the appropriate alkylolithium in diethyl ether. The resulting heteroleptic alkylberyllium complexes were extracted from the lithium chloride byproduct into hot toluene because of their poor solubility in other hydrocarbon solvents. ¹H NMR spectroscopic data showed a sharp upfield (3H) Be–CH₃ singlet resonance at –1.07 ppm for compound 3 and a diagnostic (2H) Be–CH₂ multiplet at –0.39 ppm for compound 4. Similarly, ¹³C{¹H} NMR spectra of compounds 3 and 4 displayed characteristic upfield resonances at –9.5 and –3.3 ppm for the beryllium-bound methyl and methylene carbon atoms, respectively. Because of broadening caused by coupling to the adjacent quadrupolar ⁹Be nucleus, the assignment of these two ¹³C resonances had to be confirmed by an additional HMQC experiment. For comparison, the analogous dimeric methylmagnesium β-diketiminato species displays similar

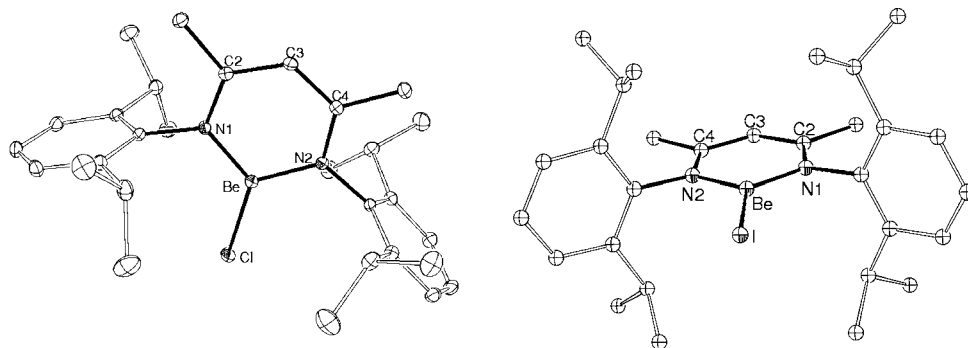


Figure 1. ORTEP representations of complexes 1 (left) and 2 (right). Thermal ellipsoids at 20% probability. Hydrogen atoms omitted for clarity.

Table 1. Details of the X-ray Diffraction Experiments of Complexes 1–5, 7, 8, 11, 12, and 14a/14b

	1	2	3	4	5	7	8	11	12	14a/14b
molecular formula	C ₂₉ H ₄₁ BeClN ₂	C ₂₉ H ₄₁ BeIN ₂	C ₃₀ H ₄₄ BeN ₂	C ₃₃ H ₅₀ BeN ₂	C ₃₅ H ₄₂ BeN ₂ O	C ₃₃ H ₅₀ BeN ₂ O	C ₃₅ H ₄₆ BeN ₂ O	C ₃₅ H ₄₇ BeN ₃	C ₃₅ H ₅₉ BeN ₃ Si ₂	C ₆₃ H ₁₂₆ Be ₃ Cl ₂ K ₂ N ₄ O ₁₂
fw (g mol ⁻¹)	462.10	553.55	441.68	483.76	443.66	495.76	519.75	518.77	587.04	1529.81
cryst. syst.	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	orthorhombic
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n	P2 ₁ /a	P 2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P1	Pcab
a (Å)	12.5670(3)	12.38820(10)	12.5290(5)	10.8395(1)	12.6193(2)	17.2222(2)	8.8001(2)	18.2273(8)	9.1722(1)	18.2948(2)
b (Å)	16.2125(3)	17.2714(2)	16.5067(9)	20.6665(3)	16.0927(4)	9.01020(10)	17.9041(5)	8.6294(4)	10.5996(2)	18.8402(3)
c (Å)	13.8581(4)	13.87650(10)	13.8582(5)	13.8904(2)	13.7326(3)	20.3315(3)	20.3625(6)	40.260(2)	20.4390(4)	25.1512(4)
α (deg)	90	90	90	90	90	90	90	90	90	90
β (deg)	104.430(1)	104.2280(10)	104.395(3)	93.982(1)	104.4351(13)	91.8612(5)	90	99.0372(14)	92.382(1)	90
γ (deg)	90	90	90	90	90	90	90	90	114.454(1)	90
V (Å ³)	2734.41(11)	2877.96(5)	2776.1(2)	3104.14(7)	2700.76(10)	3153.29(7)	3208.27(15)	6254.0(5)	1805.28(5)	8669.1(2)
Z	4	4	4	4	4	4	4	8	2	4
ρ (g cm ⁻³)	1.122	1.278	1.057	1.035	1.091	1.053	1.076	1.102	1.080	1.172
μ (mm ⁻¹)	0.158	1.130	0.060	0.058	0.064	0.062	0.063	0.063	0.124	0.229
θ range (deg)	3.94–27.53	3.03–34.95	3.53–27.54	3.75–27.39	3.93–27.55	3.01–27.48	3.81–27.48	4.08–25.09	3.84–27.47	4.05–27.49
R1, ^a wR2	0.0388, 0.0942	0.0292, 0.0684	0.0605, 0.1131	0.0619, 0.1638	0.0455, 0.1083	0.0487, 0.1149	0.0508, 0.1024	0.0499, 0.1137	0.0386, 0.1000	0.0581, 0.1389
[I > 2σ(I)] ^b	0.0572, 0.1063	0.0465, 0.0766	0.1833, 0.1537	0.0805, 0.1798	0.0698, 0.1222	0.0666, 0.1259	0.1058, 0.1226	0.0993, 0.1323	0.0413, 0.1023	0.1078, 0.1635
R1, wR2 (all data) ^b	0.0572, 0.1063	0.0465, 0.0766	0.1833, 0.1537	0.0805, 0.1798	0.0698, 0.1222	0.0666, 0.1259	0.1058, 0.1226	0.0993, 0.1323	0.0413, 0.1023	0.1078, 0.1635
measd/indep reflns/ ^c R _{int}	41758/6255/0.0562	69427/12562/0.0491	37521/6338/0.1368	47341/6992/0.0439	50421/6163/0.0641	51158/7208/0.0655	51955/6985/0.0955	51682/10829/0.0778	22925/7392/0.0306	137933/9913/0.0877

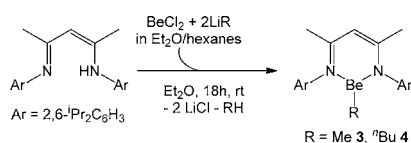
$$^a R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^b wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2}.$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1–5, 7, 8, 11, and 12

	1	2	3	4	5	7	8	11	12
Be–N1	1.6107(19)	1.6032(18)	1.631(3)	1.637(2)	1.6381(18)	1.6455(17)	1.629(4)	1.623(3)	1.6983(18)
Be–N2	1.6119(19)	1.6046(18)	1.641(3)	1.633(2)	1.6361(19)	1.6420(17)	1.607(4)	1.643(3)	1.6609(19)
Be–X	1.9041(17) ^a	2.2872(15) ^b	1.720(4) ^c	1.702(3) ^c	1.5059(19) ^d	1.4457(17) ^d	1.455(5) ^d	1.572(3) ^e	1.6160(17) ^e
N1–C2	1.3427(17)	1.3429(14)	1.340(3)	1.337(2)	1.3387(16)	1.3395(14)	1.328(3)	1.348(2)	1.3416(15)
N2–C4	1.3398(17)	1.3420(14)	1.342(3)	1.3407(19)	1.3371(16)	1.3332(15)	1.347(3)	1.332(2)	1.3446(15)
C2–C3	1.3942(18)	1.3975(16)	1.394(3)	1.399(2)	1.3950(18)	1.3968(16)	1.398(4)	1.384(2)	1.3921(18)
C3–C4	1.3954(18)	1.3991(16)	1.388(3)	1.392(2)	1.3967(17)	1.3967(16)	1.390(4)	1.397(2)	1.3928(17)
Be–N1–C2	120.31(11)	119.27(10)	121.89(18)	122.45(13)	121.40(10)	122.12(9)	120.70(19)	121.19(14)	119.76(10)
Be–N2–C4	119.85(11)	119.56(10)	121.84(18)	122.21(12)	121.59(10)	122.72(9)	121.01(19)	121.79(14)	120.39(10)
N1–C2–C3	121.28(11)	121.72(10)	121.1(2)	120.99(14)	121.49(11)	121.48(10)	121.7(2)	121.59(15)	121.75(11)
N2–C4–C3	121.84(12)	121.39(10)	120.97(19)	121.36(13)	121.38(11)	121.23(10)	121.2(2)	120.84(15)	121.33(11)
C2–C3–C4	125.06(12)	125.11(10)	125.6(2)	124.94(14)	125.15(12)	124.85(11)	124.99(16)	125.51(16)	125.66(11)
N1–Be–N2	111.66(11)	112.95(10)	108.5(2)	108.00(13)	108.97(11)	107.58(10)	110.36(15)	109.02(15)	107.66(9)
N1–Be–X	124.62(10) ^a	123.47(9) ^b	125.8(2) ^c	122.09(13) ^c	126.94(12) ^d	129.85(11) ^d	122.1(7) ^d	134.04(17) ^e	126.26(11) ^e
N2–Be–X	123.72(10) ^a	123.58(9) ^b	125.6(2) ^c	129.62(14) ^c	124.09(12) ^d	122.44(11) ^d	127.5(7) ^d	116.77(15) ^e	125.93(11) ^e

^aX = Cl. ^bX = I. ^cX = C30. ^dX = O. ^eX = N3.

Scheme 2



upfield metal-bound methyl resonances at $\delta_{1\text{H}}$ -1.17 and $\delta_{13\text{C}}$ -18.6 ppm.¹¹ Analogous alkyl complexes of the heavier alkaline earths remain unknown because of their high thermal instability. ⁹Be NMR resonances were shifted downfield from the halides **1** and **2** to 16.6 and 14.9 ppm for compounds **3** and **4**, respectively. Colorless crystals of compounds **3** and **4** suitable for X-ray structural analysis were isolated in good yield (72% and 81%, respectively) from concentrated toluene solutions at room temperature. The results of these experiments are displayed in Figure 2. Details of the X-ray analyses and selected bond length and angle data are provided in Tables 1 and 2, respectively.

In contrast to their magnesium analogues, compounds **3** and **4** were found to be monomeric both in the solid state and in solution. As for the halide complexes, the C₃N₂Be six-membered ring formed by the ligand backbone in both complexes **3** and **4** is perfectly planar, with the beryllium-bound C30 atoms lying in the same plane. The Be–C30 bond lengths [**3**, 1.720(4) Å; **4**, 1.702(3) Å] are marginally shorter than those observed for a recently reported, and similarly three-coordinate, dimethylberyllium

N-heterocyclic carbene complex [IPrBeMe₂] [1.734(2) and 1.749(2) Å].¹² The *n*-butyl chain of complex **4** also lies close to the plane of the C₃N₂Be β -diketiminato framework, with a maximum deviation of 0.29 Å from this plane for C30, and to the best of our knowledge, complex **4** is the first structurally characterized *n*-butylberyllium derivative. In both compounds, a space-filling view reveals the beryllium center to be tightly encapsulated by the 2,6-diisopropylphenyl ligand substituents and the methyl or *n*-butyl fragments, respectively. As a result, complexes **3** and **4** are relatively air-stable, and monitoring by ¹H NMR of C₆D₆ solutions of these compounds exposed to air showed only minimal hydrolysis over a 24 h period at room temperature (14% and <5%, respectively).

Synthesis of Beryllium Alkoxides. Surprisingly, the alkyl complexes **3** and **4** did not react with phenylsilane or phenylacetylene even after prolonged heating at 120 °C in toluene-*d*₈. By contrast, the controlled addition of a stoichiometric amount of degassed water in THF to a solution of **3** in THF at room temperature resulted in the slow liberation of methane gas and the clean formation of the hydroxide complex [LBeOH] (**5**; Scheme 3).

Under strictly stoichiometric conditions, no protonolysis of the β -diketiminato ligand was observed. The *n*-butyl complex **4** proved surprisingly resilient to deliberate hydrolysis, with the reaction requiring mild heating at 50 °C to achieve any significant conversion to **5**. Complex **5** exhibits a characteristic upfield

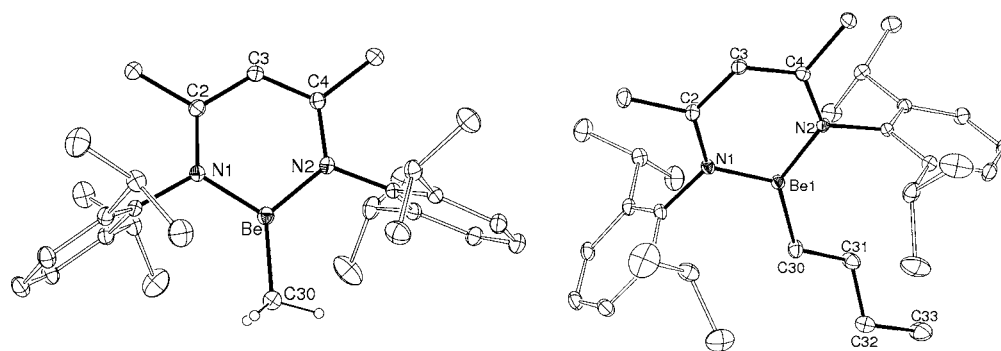
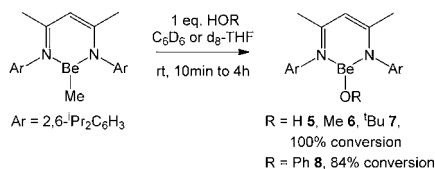


Figure 2. ORTEP representations of complexes **3** (left) and **4** (right). Thermal ellipsoids at 20% probability. Hydrogen atoms omitted for clarity, except for the beryllium-bound methyl group in **3**.

Scheme 3



^1H NMR singlet resonance at 0.20 ppm for the BeOH proton. This is in agreement with the general trend displayed by the analogous THF-solvated heavier alkaline-earth β -diketiminato hydroxide dimers (complex **I**, -0.46 ppm; 3c complex **II**, -0.78 ppm; 4c complex **III**, -0.72 ppm 5b). As expected, the ^9Be NMR resonance at 8.0 ppm was shifted upfield from those in compounds **1–4** because of the shielding effect of the electron-donating nature of the beryllium-bound oxygen atom.

Large single crystals of compound **5** suitable for X-ray crystallographic analysis were obtained from a saturated THF solution at room temperature. The results of this experiment are displayed in Figure 3, and details of the X-ray analysis and

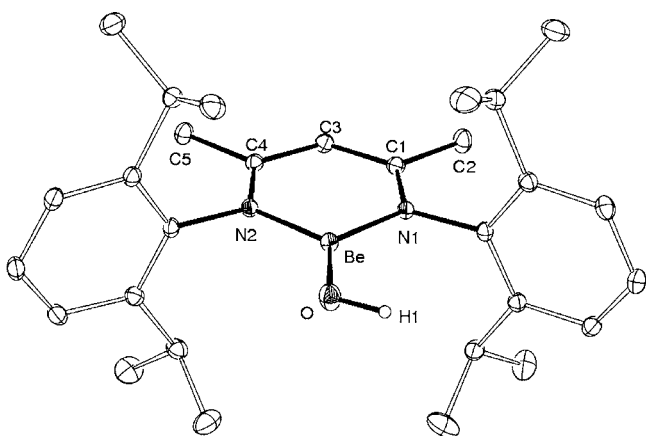


Figure 3. ORTEP representation of complex **5**. Thermal ellipsoids at 20% probability. Hydrogen atoms omitted for clarity, except for the beryllium-bound hydroxide group.

selected bond length and angle data are provided in Tables 1 and 2, respectively. The quality of the diffraction data was such that it also allowed the location and refinement of the hydroxide proton with an O–H bond length of 0.98(2) Å. As for the β -diketiminato complexes described above, the ligand framework, beryllium atom, and the hydroxyl oxygen atom all

lie in the same plane. Previous reports of beryllium hydroxide complexes with N-donor ligands include a series of tris(pyrazolyl)boratoberyllium hydroxide trimers by Sohrin et al. in which the tris(pyrazolyl)borate ligands adopt a bidentate coordination with one pendant pyrazole fragment and displaying a central $\text{Be}_3(\text{OH})_3$ six-membered ring with Be–O distances of 1.564(4)–1.595(4) Å. 13 Complex **5** is the first crystallographically characterized three-coordinate terminal beryllium hydroxide. The Be–O bond length of 1.5059(19) Å is thus the shortest reported to date for a beryllium hydroxide. Owing to the small radius of the beryllium dication, complex **5** is virtually air-stable and is the only β -diketiminato group 2 hydroxide complex to crystallize as an unsolvated monomer.

Reactions between compound **3** and methanol or *tert*-butanol provided quantitative conversion to monomeric compounds $[\text{LBeOMe}]$ (**6**) and $[\text{LBeO}^t\text{Bu}]$ (**7**) within 1 and 4 h at room temperature, respectively, as determined by NMR spectroscopy (Scheme 3). In contrast, analogous reactions using the *n*-butyl precursor **4** required heating at 80 °C for 1 and 5 h, respectively, to achieve quantitative conversions. Both alkoxides displayed characteristic γ -CH ligand backbone ^1H NMR singlet resonances around 5.13–5.17 ppm, upfield from those of the halide and alkyl derivatives. Additionally, the ^1H NMR spectra showed clean single resonances at 3.06 ppm (3H) for the methoxy ligand and 0.76 ppm (9H) for the *tert*-butoxy ligand. Although the reaction of **3** with phenol also resulted in the rapid evolution of methane and ^1H NMR data showed complete consumption of phenol within 1 h at room temperature, only 84% conversion to the desired beryllium phenoxide complex $[\text{LBeOPh}]$ (**8**) was obtained because of competitive protonation of the β -diketiminato ligand by the acidic phenol reagent. The reaction was also accompanied by the precipitation of small amounts of insoluble material deemed to be polymeric $[\text{Be}(\text{OPh})_2]_n$. ^9Be NMR spectra of the beryllium methoxide and phenoxide species showed broad resonances around 8 ppm similar to that of the hydroxide complex **5**, whereas the *tert*-butoxide resonance was shifted upfield to ca. 6 ppm.

Single crystals of compounds **7** and **8** suitable for X-ray crystallographic analysis were obtained from saturated hexane/toluene (9:1) solutions after storage at -30 °C. The results of these experiments are displayed in Figure 4. See Table 1 for details of the X-ray analyses and Table 2 for selected bond length and angle data. The crystal structure of complex **8** displayed a disorder in the beryllium-bound oxygen atom over two positions in a 84:16 ratio, the first lying in the plane of the $\text{C}_3\text{N}_2\text{Be}$ framework and the second situated 0.5 Å above, most likely due to crystal packing effects. The Be–O bond length of

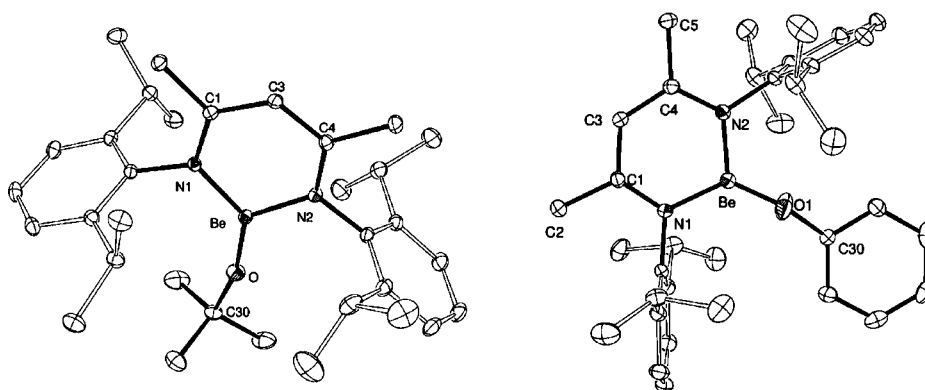


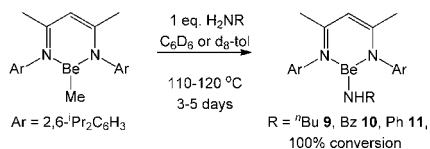
Figure 4. ORTEP representations of complexes **7** (left) and **8** (right). Thermal ellipsoids at 20% probability. Hydrogen atoms omitted for clarity.

the phenoxide derivative, compound **8** [Be–O1A 1.445(18) Å; Be–O1 1.455(5) Å] is identical with that of the bulkier *tert*-butoxide analogue [1.455(5) Å], despite the greater acidity of the phenol conjugate acid. Both sets of measurements are, however, significantly shorter than the corresponding hydroxide Be–O bond length in complex **5** [1.5059(19) Å]. In both complexes **7** and **8**, the Be–O–C30 angle approaches 180°, although more so in the phenoxide species [**7** 162.34(11)°; **8** 173(2)°], indicating a high degree of oxygen p-orbital involvement in the bonding to the beryllium center. The only previous crystallographically characterized beryllium *tert*-butoxide complexes reported to date are [Be₃(O^tBu)₄X₂] trimers (X = Cl, BH₄) and a [(Et₂O)Be(O^tBu)Br]₂ dimer with bridging *tert*-butoxide groups, in which the beryllium centers exhibit *pseudotetrahedral* geometry, which, in turn, leads to longer Be–O distances ranging between 1.54 and 1.64 Å.¹⁴ The Be–O bond length of compound **8** is comparable to that in the homoleptic phenoxide diethyl ether solvate [{2,4,6-^tBu₃-C₆H₂O}₂Be(OEt₂)] reported by Power and co-workers [1.481(2) Å], in which the beryllium atom is also effectively trigonal planar.¹⁵ Interestingly, the phenyl substituent in compound **8** is also perfectly coplanar with the β -diketiminato ligand backbone.

Despite multiple attempts, X-ray-quality crystals of the methoxide derivative **6** could not be obtained. Heating one sample of **6** in C₆D₆ at 80 °C for 1 h, however, resulted in the formation of a few small colorless crystals. An X-ray diffraction experiment performed on these crystals yielded the structure of complex **6'**, a β -diketiminato beryllium methoxide dimer bridged by a dimeric [Be(OMe)₂]₂ unit (see Figure S1 in the Supporting Information). Although no evidence for the homoleptic species [L₂Be] could be found in the ¹H NMR spectra, it must be assumed that complex **6** underwent Schlenk-type equilibration and that the resulting homoleptic [Be(OMe)₂]₂ dimer was trapped by complex **6** to form this unusual Be₄ complex. Although poor diffraction at angles above 22.5° precludes any meaningful structural discussion, complex **6'** is, to our knowledge, the first beryllium complex containing four aligned beryllium atoms. Unfortunately, the small amount of isolated crystalline material did not facilitate further characterization of this compound.

Synthesis of Beryllium Amides. While hindered amines such as hexamethyldisilazane and *tert*-butylamine did not undergo deprotonation with complex **3**, less hindered substrates such as *n*-butylamine and benzylamine reacted slowly (2–5 days) with **3** at 110 °C in toluene to form [LBe{NH^tBu}] (**9**) and [LBe{HNCH₂Ph}] (**10**; Scheme 4). The ¹H NMR spectra

Scheme 4



of these compounds exhibited characteristic triplet signals at –0.21 and 0.19 ppm, respectively, attributed to the BeNH resonances. For comparison, the related heavier group 2 amide complexes [LM{NHCH₂Ph}] (M = Mg, Ca) displayed ¹H NMR NH resonances at –0.52 and –0.45 ppm, respectively.¹⁶ Both complexes displayed very high solubility in hexanes even at –30 °C as well as extreme sensitivity to hydrolysis, preventing the isolation of clean bulk crystalline material for elemental analysis and X-ray diffraction experiments.

The reaction between compound **3** and aniline at 120 °C also led to quantitative conversion over 3 days to the monomeric [LBeNHPh] (**11**), the ¹H NMR spectrum of which displayed a characteristic NH singlet at 2.96 ppm overlapping with the isopropyl resonance of the β -diketiminato ligand. Similarly, ¹H NMR data of the related complex [LCa{NH(2,6-ⁱPr₂C₆H₃)}(THF)] has been reported to display a NH singlet resonance at 3.36 ppm in C₆D₆,¹⁷ while the corresponding NH shift in the heteroleptic anilidomagnesium dimer [Mg(NHPh){N(SiMe₃)₂}]₂ appeared at 3.62 ppm.¹⁸ Single crystals of the anilido complex **11** were obtained from concentrated toluene solutions at –30 °C. The results of the X-ray crystallographic experiment are displayed in Figure 5. As before, relevant structural data are provided in Tables 1 and 2. The complex crystallizes as a mixture of two structurally distinct monomeric molecules, both of which present a distorted trigonal-planar beryllium center and Be–N_{anilido} bond lengths of 1.572(3) and 1.577(3) Å, respectively. The latter distances are considerably shorter than those in the terphenylberyllium anilide complex reported by Power and co-workers, which crystallized as a dimer with trigonal coordination at beryllium and Be–N bond lengths ranging from 1.690(6) to 1.725(6) Å.¹⁰ The quality of the diffraction data allowed the location and free refinement of the anilido NH proton [N3–H3 0.901(18) Å], confirming the trigonal-planar configuration of the anilido nitrogen atom. Despite the very different steric demands of the 2,6-diisopropylanilide ligand compared to the parent anilide, the M–N3–C30 angle in beryllium complex **11** [M = Be, 143.04(16)°] is very similar to that in the aforementioned β -diketiminato calcium complex [M = Ca, 143.00(15)°].¹⁷ Interestingly, the phenyl ring of the anilide coligand is not quite coplanar with the β -diketiminato backbone, with the two planes forming an angle of 13.5°.

A one-pot salt metathesis procedure that has previously been employed to synthesize the analogous calcium complex [LCa{N(SiMe₃)₂}(THF)] was used in an attempt to synthesize β -diketiminatoberyllium bis(trimethylsilyl)amide. After removal of THF, extraction into hot toluene, and concentration in vacuo, however, only a small amount of the desired [LBe{N(SiMe₃)₂}] (**12**) complex was obtained as needlelike colorless crystals (21% yield). The solid residues from the toluene extraction proved insoluble in C₆D₆ and toluene-*d*₈, indicating they did not contain complex **12**. A subsequent synthesis using salt metathesis between the iodo complex **2** and [K{N(SiMe₃)₂}] resulted in failure to isolate any complex **12**. Repetition of this reaction on an NMR scale in toluene-*d*₈ indicated that, as well as inducing the anticipated salt metathesis, [K{N(SiMe₃)₂}] had deprotonated one of the β -methyl functionalities of the β -diketiminato ligand in a manner reminiscent of the heavier alkaline-earth dialkyls [M{CH(SiMe₃)₂}(THF)₂] (M = Ca, Sr, Ba)¹⁹ to form KI and a diamidoberyllium complex (Scheme 5), identified by the two characteristic methylene *cis* and *trans* ¹H NMR resonances at 3.45 and 2.46 ppm (shown to couple by COSY) and the asymmetric isopropyl septets at 3.76 and 3.71 ppm. The latter species precipitated over a period of 2 h at room temperature and proved insoluble even in boiling toluene, precluding any further analysis. Isolated crystals of **12** also underwent complete decomposition into a brown tarlike product over a period of 2 days even under an argon atmosphere, preventing the acquisition of elemental analysis data. Single crystals of compound **12** were, however, obtained from the first synthetic method. The results of this X-ray crystallographic experiment are displayed in Figure 5, while details of the X-ray analysis and selected bond length and angle data are provided in Tables 1 and 2, respectively. Complex **12** is

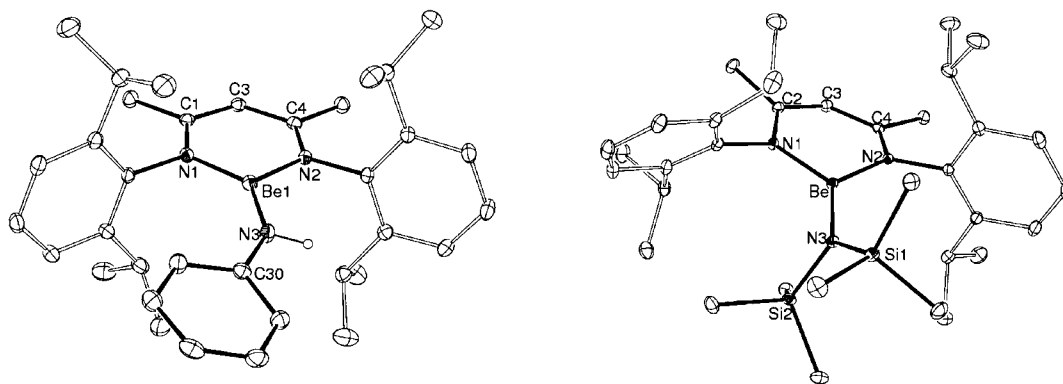
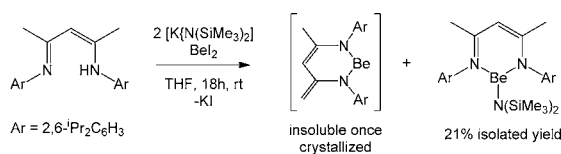


Figure 5. ORTEP representations of complex **11** (left) and one of the two distinct molecules present in the unit cell of **12** (right). Thermal ellipsoids at 20% probability. Hydrogen atoms omitted for clarity except the anilide proton H3.

Scheme 5



the only one of the compounds described herein to present a nonplanar ligand backbone in which the β -diketiminato adopts a boat-type conformation, with the beryllium atom lying ca. 0.23 Å above the mean plane of the ligand. Although the beryllium center is still three-coordinate, the N–Be–N coordination plane subtends an angle of ca. 15° with the mean plane of the ligand backbone, in order to accommodate the sterically demanding bis(trimethylsilyl)amide ligand. The only two other crystallographically characterized beryllium bis(trimethylsilyl)amide complexes, a monomeric terphenyl complex and a diberyllium dichloro(amidinate) complex with a bridging $\{N(SiMe_3)_2\}^-$ ligand, were reported by Power and co-workers.^{10a} The former two-coordinate linear beryllium species displayed a Be–N_{amido} bond length of 1.519(4) Å, while the latter complex, with a *pseudo*-tetrahedral geometry around beryllium, had Be–N_{amido} bond lengths of 1.686(5) and 1.671(5) Å. As expected, the corresponding bond length in the trigonal-planar complex **12** [1.6160(17) Å] is intermediate between these two extremes.

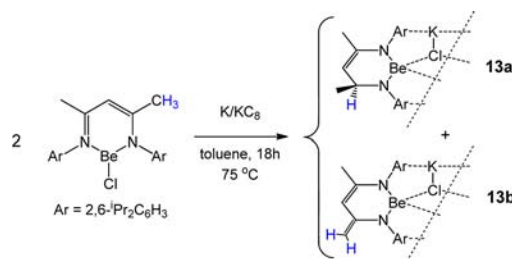
Reduction of β -Diketiminatoberyllium Complexes.

Encouraged by Jones and co-workers' report of the reduction of $[LMgI]$ and related heteroleptic magnesium iodide complexes to form $[LMgMgI]$ dimers containing two formally Mg^I centers, reduction of the beryllium halides **1** and **2** was attempted. The reaction of **1** with 1 equiv of potassium metal at 75 °C in toluene overnight resulted in the complete consumption of potassium and the formation of a clear pale-yellow solution. Hot filtration followed by slow crystallization at room temperature yielded a crop of large colorless crystals suitable for X-ray diffraction analysis. Despite multiple recrystallization attempts from a variety of hydrocarbon solvents, the structure of the complex was always disordered around a mirror plane, with large amounts of highly disordered residual solvent in the lattice, which could not be modeled satisfactorily. Although a detailed structural discussion is therefore precluded, the apparent atomic connectivity of the molecule was established and found to be suggestive of an β -diketiminatoberyllium chloride dimer including potassium cations stabilized by π interactions with the pendant *N*-aryl groups (see Figure S2 in the Supporting Information). For maintenance of the charge

balance, it was deduced that the coordinated β -diketiminates had undergone reduction and were thus coordinated as diamide ligands.

Thorough analysis of the collated NMR data (¹H, COSY, ¹³C{¹H}, HMQC, and HMBC) recorded from a sample of isolated crystals revealed that reduction of compound **1** had indeed occurred (Scheme 6). The potassium reduction reaction

Scheme 6



was deduced to have resulted in the formation of a mixture of two distinct diamidoberyllium species, **13a** and **13b**, which were present in solution as a statistical mixture of the three possible, but spectroscopically indistinguishable, dimeric (**13a/13a**, **13b/13b**, and **13a/13b**) molecules. In **13a**, this process resulted in the apparent hydride reduction of the ligand imine functionality, while in **13b**, a dianionic constitution was achieved by the transformation of one of the ligand backbone methyl groups to a methylene substituent. Figure 6 illustrates an annotated ¹H NMR spectrum of a crystalline sample recorded in THF-*d*₈, where the shifts of the β and γ protons of the diamido ligand backbone of complex **13a** were observed to overlap at 4.04 ppm. The methyl substituent of the sp³ β carbon was identified by a COSY experiment at 1.11 ppm. The 3:2 ratio of **13a** and **13b** in the crystalline product may be explained by the higher solubility of **13b** in toluene, causing dimeric species containing **13a** to crystallize preferentially. Subsequent *in situ* monitoring of the same reaction by ¹H NMR spectroscopy showed that both compounds were actually formed in equimolar quantities as the sole final products of the reaction.

The addition of 2 mol equiv of 18-crown-6 to a suspension of **13a/13b** caused instantaneous dissolution in C₆D₆, while crystallization at room temperature afforded large colorless crystals of the crown-adduct mixture **14a/14b**. The results of this X-ray crystallographic experiment are displayed in Figure 7, and details of the X-ray analysis are provided in Table 1. In this case, the X-ray diffraction data were of sufficient quality so as

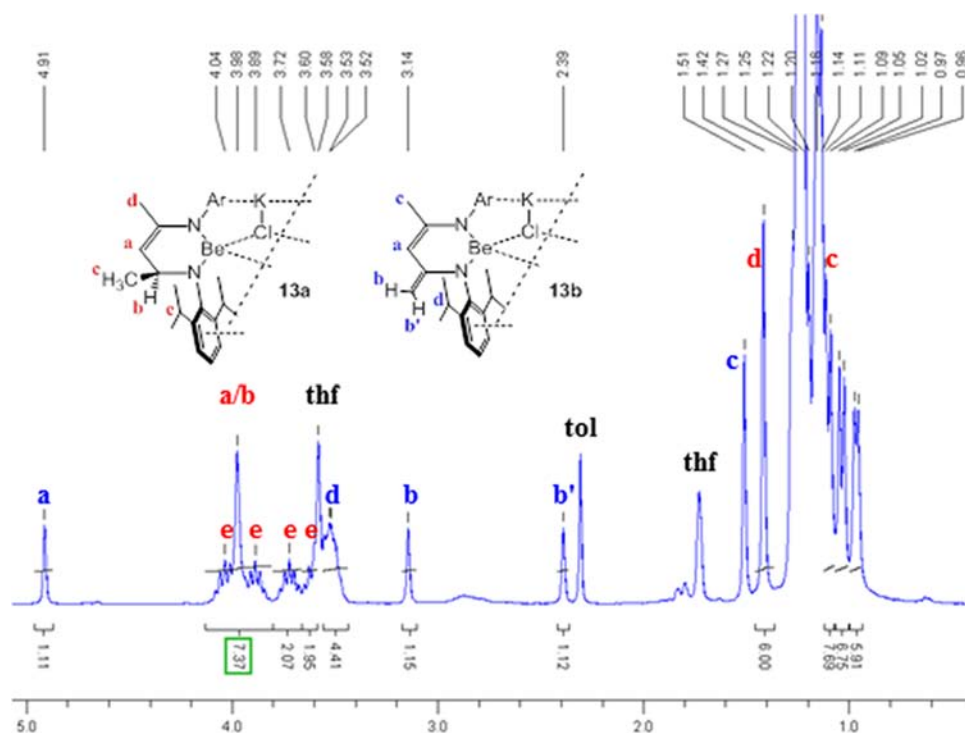


Figure 6. Annotated ^1H NMR spectrum of a crystalline sample of a 3:2 mixture of 13a and 13b in $\text{THF-}d_8$.

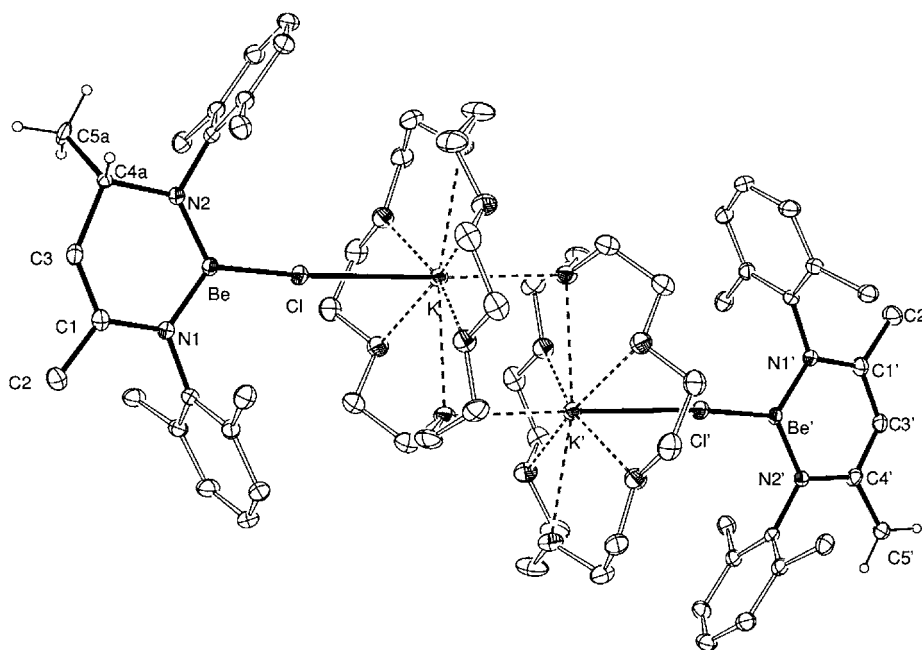


Figure 7. ORTEP representation of the mixed complex 14a/14b, with the left half of the dimer showing the geometry of complex 14a and the right half that of complex 14b. Thermal ellipsoids at 20% probability. Isopropylmethyl groups and hydrogen atoms omitted for clarity except those on the sp^3 β carbon C4a and the adjacent methyl group (C5) and those on the methylene carbon C5'. Primed labeled atoms are related to those in the asymmetric unit by the $2 - x, 1 - y, 2 - z$ symmetry operation.

to allow the structure of 14 to be successfully modeled as a 1:4 ratio of the two diamide complexes. The mixture thus crystallizes as a $[\text{L}_{a/b}\text{BeClK}\{18\text{-crown-}6\}]_2$ dimer (L_a = protonated diamido ligand; L_b = deprotonated diamido ligand), formed by two three-coordinate diamidoberyllium complexes and two crown-ether-complexed potassium chloride units bonding to the beryllium atoms via $\text{Be}-\text{Cl}-\text{K}$ bridging interactions.

The two molecules of the dimer are bound to one another by interactions between the potassium cations and the oxygen atom O3 of the second crown ether molecule. The four atoms $\text{Be}-\text{Cl}-\text{K}-\text{O}3'$ are aligned in a near-linear fashion in the same plane as the ligand framework, with $\text{Be}-\text{Cl}-\text{K}$ and $\text{Cl}-\text{K}-\text{O}3'$ angles of $174.84(10)$ and $173.40(5)^\circ$, respectively. The $\text{Be}-\text{Cl}$ bond length [$1.951(3)$ Å] is slightly elongated compared to that of the parent species 1 [$1.9041(17)$ Å] because of the

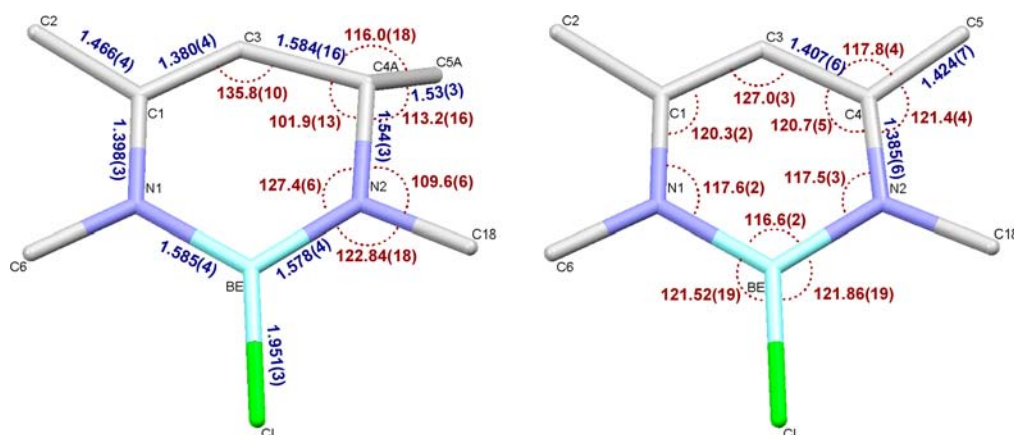


Figure 8. Comparison of the bond lengths (blue, Å) and angles (red, °) of the ligand frameworks in complexes **14a** and **14b**. The bond lengths and angles on the N1–C1–C2 side of the molecule are similar in **14a** and **14b**.

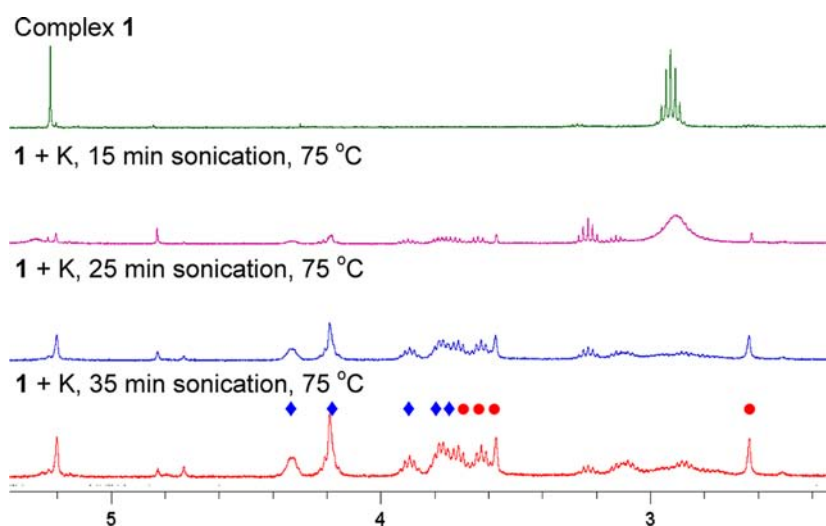


Figure 9. ^1H NMR stack plot monitoring the in situ reaction of complex **1** with potassium metal in toluene- d_8 (blue \blacklozenge , complex **13a**; red \bullet , complex **13b**).

additional K–Cl interaction. Figure 8 shows the core frameworks of **14a** and **14b** for a clearer comparison of bond lengths and angles in both species. The N–Be–N angle [$116.6(2)^\circ$] is considerably more obtuse and the Be–N bonds are shorter [$1.585(4)$ and $1.578(4)$ Å] in both diamido species than in the related complex **1** [N–Be–N $111.66(11)^\circ$; Be–N $1.6107(19)$ and $1.6119(19)$ Å], as expected from the dianionic nature of the diamide ligands. Although the six-membered ring formed by the ligand backbone and the beryllium atom remains relatively planar in both **14a** and **14b**, the bond lengths and angles deviate significantly from those in complex **1**. From the bond distances in **14b**, it is clear that C1–C3 has become a localized double bond [$1.380(4)$ Å], while the C3–C4A distance of $1.584(16)$ Å is indicative of a single bond. This situation is similar to that observed in the germanium(II) complex [$\{\text{MesNC}(\text{tBu})=\text{CHCH}(\text{tBu})\text{NMes}\}\text{Ge}$] (Mes = 2,4,6-trimethylphenyl), reported by Jones and co-workers, which exhibited analogous bond lengths of $1.344(2)$ and $1.510(2)$ Å.²⁰ Similarly, the C4A–N2 bond in complex **14a** shows clear signs of being a localized single bond [$1.54(3)$ Å]. Because of the sp^3 hybridization of the C4A carbon center, the C4A–C5A single bond [$1.53(3)$ Å] does not lie in the plane of the ligand framework. The angles of the $\text{C}_3\text{N}_2\text{Be}$ ring also undergo considerable distortion, with a widening of the C1–C3–C4A and Be–N2–C4A angles

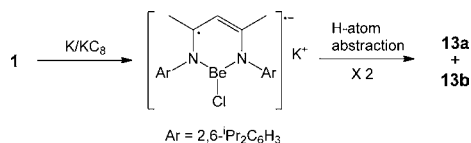
[$135.8(10)$ and $127.4(6)^\circ$, respectively] compared to complex **1** and a dramatic narrowing of the N2–C4A–C2 angle from ca. 121° in complex **1** to ca. 102° in complex **14a**. In contrast, the ligand backbone structure of complex **14b** shows a greater degree of delocalization, with similar C–N bond lengths [$1.398(3)$ and $1.385(6)$ Å] and only a slight shortening of the alkenic C4–C5 bond [$1.424(7)$ Å] compared to the C1–C2 single bond [1.466 Å].

To provide some insight into the formation of **13a/13b**, a reaction between complex **1** and potassium metal was sonicated at 75°C in toluene- d_8 and monitored by ^1H NMR and ^1H – ^9Be HMQC NMR spectroscopy (Figure 9). The ^1H NMR data evidenced the rapid disappearance of the chloride complex **1**, while the appearance of the reduction products **13a** and **13b** was accompanied by several unidentified reaction intermediates and a dark-blue color, which faded upon heating. Similar transient color changes have been observed by Jones and co-workers during their attempts to reduce the β -diketiminato beryllium iodide complex [$\{\text{HC}(\text{CMeNMes})_2\}\text{BeI}$] (Mes = 2,4,6-trimethylphenyl) and attributed to the formation of a highly reactive radical intermediate.⁸ It is notable that throughout the reaction **13a** and **13b** remained in a constant ratio of 1:1, suggesting a concerted mechanism of formation. While deprotonation of one of the methyl substituents on the

β -diketiminato backbone, to yield the diamide ligand observed in **13b**, has been reported by us and others in the presence of strong bases,^{19,20} hydrogen transfer onto the β -carbon position of the diketiminato framework has only been reported in two cases, in which the ligand was reduced by either $\text{BH}_3 \cdot \text{Et}_2\text{O}$ or a germanium hydride complex.^{21,22} It is notable that the $[\{\text{MesNC}(\text{tBu})=\text{CHCH}(\text{tBu})\text{NMes}\}\text{Ge}]$ complex reported by Jones and co-workers was formed by hydride transfer from a defined β -diketiminatogermanium(II) hydride complex, $[\{\text{HC}\{\text{C}(\text{tBu})\text{NMes}\}_2\}\text{GeH}]$.²⁰ ^1H - ^9Be HMQC NMR, however, showed no sign of an intermediate beryllium hydride species during the reduction process to form **13a/13b**. The reaction mixture of an analogous potassium reduction performed on the beryllium iodide complex, compound **2**, also turned blue, and monitoring of the reaction by ^1H NMR spectroscopy evidenced the formation of reduced ligand species analogous to those observed in **13a/13b**. In this latter case, however, advanced stages of the reaction were characterized by the precipitation of an intractable and hydrocarbon-insoluble colorless material, which we ascribe to the result of KI elimination from species akin to **13a/13b**.

Although the mechanism of the formation of **13a/13b** remains to be elucidated, their simultaneous appearance in situ reactions is indicative of a fast bimolecular process. We suggest, therefore, that the initial single-electron reduction of compound **1** in the reaction with potassium metal occurs with the formation of short-lived radical-anion species analogous to those previously observed by Lappert and co-workers during the potassium reduction of closely related β -diketiminato anions.²³ In this latter case, occupation of the lowest unoccupied molecular orbital (LUMO) π^* system of the ligand framework was further stabilized by the presence of phenyl substituents appended to the backbone of the ligand rather than the methyl groups of the ligand **L** employed in the current study. We propose, therefore, that the observed 1:1 ratio of **13a/13b** is the result of a rapid intermolecular hydrogen-atom-abstraction reaction that occurs between pairs of the radical-anion species (Scheme 7). While no

Scheme 7



mechanistic rationale appears to have been proposed for the formation of the magnesium(I) compounds **IV** and **V**, it appears reasonable to propose that a similar single-electron transfer to the ligand-based π^* system occurs during reduction of the magnesium iodide starting materials employed in the synthesis of both of these landmark compounds. Preliminary density functional theory calculations at the B3LYP/LAN2DZ level of theory performed on the complete beryllium and magnesium chloride complexes, $[\text{HC}\{\text{CMeNDipp}\}_2\text{MCl}]$ (M = Be, Mg), indicated that the π^* system of the β -diketiminato ligand is indeed the LUMO for both complexes. Interestingly, examination of the higher-energy virtual orbitals revealed that for both compounds a further π^* -symmetric (LUMO+6) orbital associated with M–Cl antibonding is located some 0.46 eV higher in energy when M = Be. We tentatively submit, therefore, that the formation of compounds **13a** and **13b** rather than the desired beryllium(I) compounds analogous to **IV** and **V** is a consequence of the relative accessibility of such a metal-based

orbital density, whereby the β -diketiminato ligand acts either as a conduit for single-electron reduction at the group 2 element center or as a free-radical hydrogen-abstraction reagent.

CONCLUSION

A series of heteroleptic β -diketiminatoberyllium halide, alkyl, alkoxide, and amide complexes have been isolated and characterized. As a result of the small size of the beryllium dication, unsolvated β -diketiminato complexes of even small functionalities, such as methyl and hydroxide, form as kinetically stable monomers. Reduction of the halide complex with potassium metal yielded two unusual diamidoberyllium potassium chloride complexes resulting from hydrogen-atom transfer between the reduced ligand backbones. We are currently investigating the reactivity of the latter species and will report our findings in subsequent publications.

Caution! Beryllium and its compounds are extremely toxic. Suitable precautions (e.g., use of protective clothing, a breathing apparatus, and a well-ventilated fume cupboard) should be taken for all manipulations involving them.²⁴

ASSOCIATED CONTENT

Supporting Information

Full experimental and instrument details, ORTEP representations of the structures of compounds **6'** and **13a/13b**, and CIFs for **1–5**, **7**, **8**, **11**, **12**, and **14a/14b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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